

THE EFFECT OF THE ELECTRIC DISCHARGE ON
WATER VAPOUR.

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(Plates II., III.)

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Introductory.—This research was initially undertaken with a view to verifying the results set forth by M. A. Henry in the *Journal de Physique* (tome viii., Jan., 1909, pp. 33–38), namely, that a vacuum tube containing only water vapour will show Cooke's effects at considerably higher pressures than if it contained air; *i.e.*, that the upper limit of pressure suitable for the existence of cathode rays, and consequently of Röntgen rays, is much higher in the case of water vapour than in the case of air.

At an early stage of the work, however, unexpected effects occurred, and the investigation of these rendered the original subject of research altogether secondary.

Method of Procedure.—The method of procedure and the experimental arrangements were essentially different to those of M. Henry. In principle, the method first intended to be employed was the following: An ordinary X-ray bulb, fitted with suitable means for admitting various quantities of air or water vapour, was connected to a mercury pump. Air pressures were read by a McLeod gauge, and pressures of water vapour by a manometer of the ordinary kind. Exhaustion was carried on until the bulb emitted good X-rays, and the quantity of air or water vapour necessary to cause a cessation of the emission of rays was then noted.

Methods of admitting Water Vapour.—The first method of introducing water vapour into the bulb was through a fine capillary of such small bore that air could be admitted at the rate of twenty to thirty thousandths of

a millimetre per minute when exhaustion had been carried to 0.000 mm. (*i.e.*, less than $\frac{5}{10000}$ mm.). Fig. 1 is a diagrammatic sketch, showing the arrangement. The end of the capillary is surrounded by the vapour from the boiling water in the flask F; *ll* serves to break off a short length of the capillary when vapour is required to be admitted. The bulbs B_1 , B_2 contain P_2O_5 . Connection between these bulbs and the X-ray bulb is made through mercury traps.

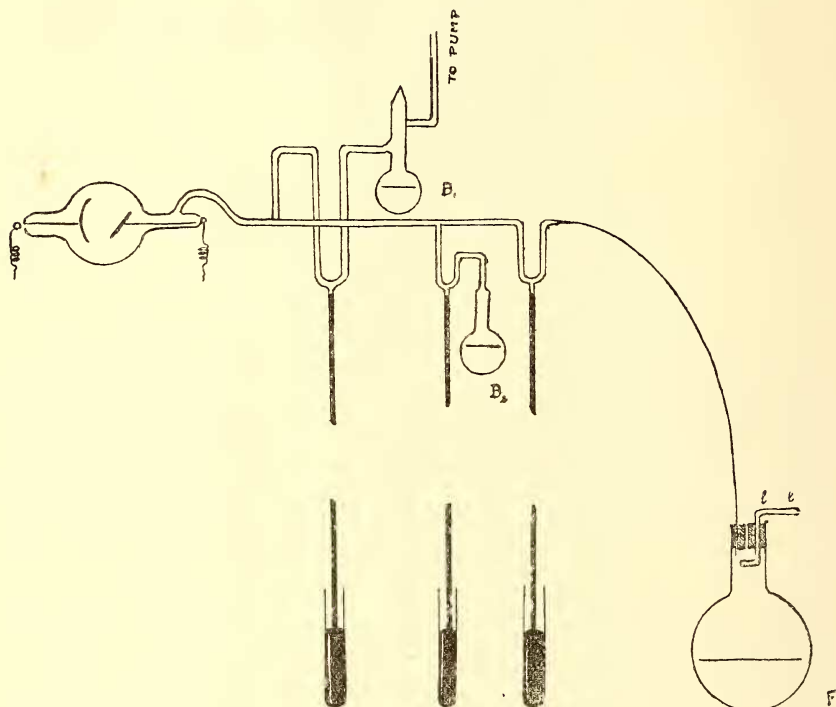


FIG. 1.

This method of introducing the vapour was found to be unsatisfactory. Some vapour or gas, unabsorbed by P_2O_5 , invariably remained after the introduced water vapour had been admitted to the P_2O_5 bulbs; the McLeod gauge indicated pressures varying from a few thousandths to a few hundredths of a millimeter.

Fig. 2 illustrates the second method of introducing vapour. The bulb W contained water and water vapour only. To introduce the vapour into the X-ray bulb, &c., the mercury was made to fall below J by lowering the reservoir R. The tube *ab* was 80 cm. long. Its

dimensions were such that if at any time it was necessary to open the apparatus (*e.g.*, to change the X-ray tube) the mercury might be made to fill the tube to such a height that the pressure in the apparatus might

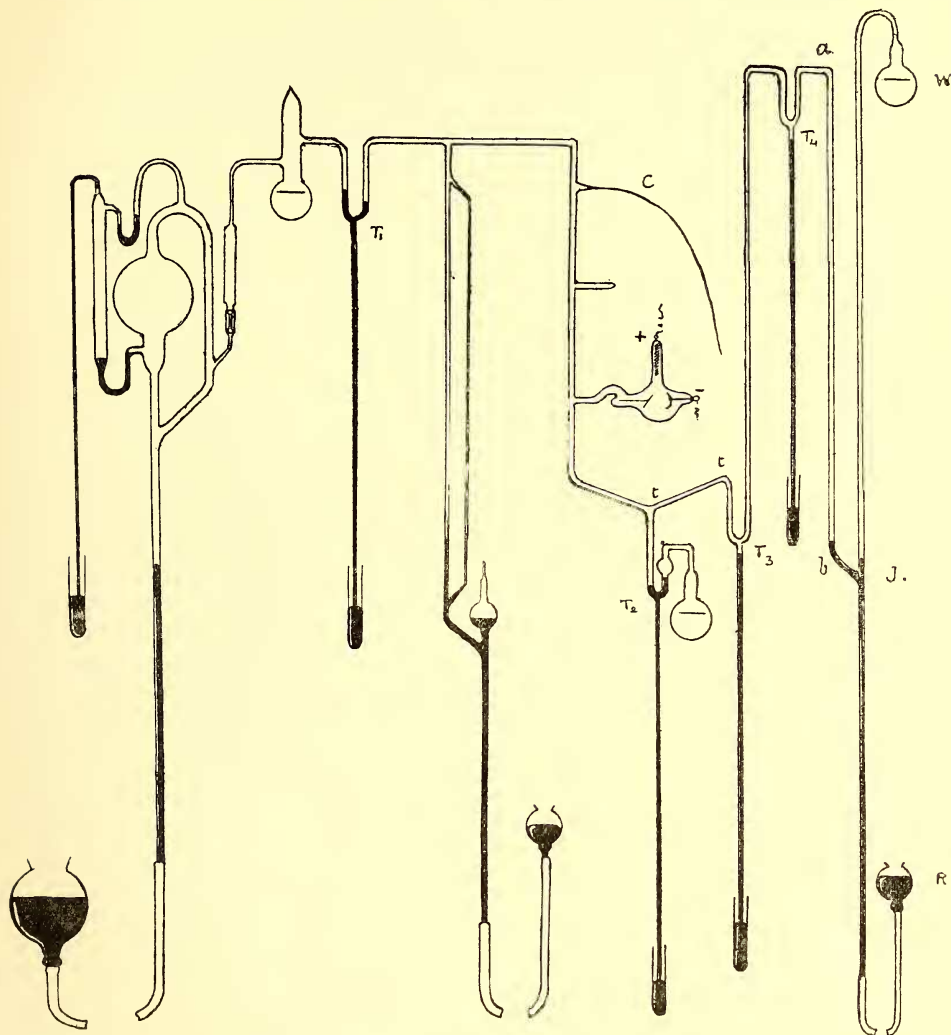


FIG. 2.

rise to one atmosphere without the mercury falling below J, so that by merely raising R sufficiently, W remained cut off and the water vapour unmixed with air.

The arrangement was connected to the remainder of the apparatus through two mercury traps separated by 80 cm. of 3-mm. bore-tubing

(see Fig. 2). The object of this was to allow of the introduction of definite small quantities of vapour into the apparatus. Vapour under various pressures ranging to saturation pressure was introduced into the exhausted apparatus and absorbed, in order to test for the presence of any unabsorbable gas carried over with the vapour. The results were satisfactory. After the first two trials the pressures indicated by the gauge after the vapour had been absorbed varied from 0.001 mm. downwards. This method of admitting vapour was adopted.

Experimental Arrangements.—Fig. 2 shows the complete apparatus as finally used. The trap T served to separate the pump and P_2O_5 bulb from the rest of the apparatus, so that the X-ray tube and the McLeod gauge might be connected without the inclusion of any P_2O_5 bulb. It also served as a manometer for measuring the pressure of vapour introduced into the X-ray tube. The capillary C was added as a means of introducing air or other gases quite independently of the introduction of water vapour. The slope of the tube *tt* was for the prevention of its obstruction by mercury carried over from the trap T_3 when this was opened for the introduction of the vapour; for at this stage the trap separated two regions of the apparatus, in one of which was a pressure of 0.000 mm., and in the other of which was saturation pressure of water vapour.

The X-ray tubes first used were of the ordinary type, with aluminium cathode and platinum anode and anticathode combined. An ordinary 10-inch spark induction coil, with platinum contact-breaker, was used for the discharge, worked by accumulators giving 8 volts. The spark-length (between points) in air was about 2.5 cm.

Experiments were first made with air. The air was admitted through the capillary, and the variation in quality of the X-rays tested by observing the sharpness and intensity of a shadow cast on a barium platino-cyanide screen. These experiments yielded no satisfactory results, the behaviour of the various tubes being very inconsistent. A characteristic inconsistency was in the reduction of pressure produced by the discharge. This phenomenon was present in most of the tubes, but it was very much more marked in some cases than in others. In one instance the discharge disposed of the air as fast as it was introduced through the capillary, so that, with the capillary broken, the tube was giving good rays for several minutes. Blackening of the tubes through the disintegration of the electrodes was rapid and considerable, more especially when the pressure of air in the tube was too high for the passage of the discharge to be attended by any fluorescence of the glass. Attempts were made to diminish this effect by varying the form of X-ray tube. The form of tube shown in Fig. 3 is that which proved to be the most successful. The anode was made in the form of a long spiral of aluminium, with the object of exposing

a large surface. The anticathode, of platinum, was not used as an electrode.

Experiments with Water Vapour.—It was found impossible to determine what pressure of vapour would cause a cessation of the emission of rays; for immediately on passing the discharge through the vapour the pressure, as indicated by the McLeod gauge, increased rapidly, showing that gas was being formed at a rapid rate, while the fluorescence of the X-ray tube ceased almost immediately.

These increases in pressure were not consistent, owing, no doubt, to variations in temperature, variations in the physical conditions in the X-ray tube, &c. In every case, however, these increases tended to a limit.

If, after gas had been formed in this way, the trap T_2 was opened, so that connection between the X-ray tube and the P_2O_5 bulb was brought about, the pressure as indicated by the gauge was found to fall at a diminishing rate as the passage of the discharge continued.

From these preliminary experiments it would appear that the effect of the discharge on small quantities of water vapour is to cause partial dissociation. A definite fraction of the vapour would become dissociated into the electrolytic gases H_2 and O_2 . If the vapour, in the meantime, remained unabsorbed, this dissociation would continue till the pressure of electrolytic gas attained to a steady value. If, however, the vapour, which would still exist undissociated, were now absorbed, the pressure conditions would no longer be in equilibrium. Some of the electrolytic gas would recombine to form H_2O ; but as fast as this recombination took place, the water would be absorbed by the P_2O_5 , a steady state of pressure would no longer be possible, and the pressure indicated by the McLeod gauge would fall off with time.

Reduction Effect.—After the above experiments with water vapour had been conducted, it was found that immediately on introducing any water vapour, gas began to be formed, quite independently of the passage of any discharge. The pressure as indicated by the McLeod gauge increased steadily to a maximum and permanent value. This effect seems to have been due directly to some change in the internal condition of the X-ray tube brought about by the passage of the previous discharges.

The effect grew rapidly with time. Thus, five days after the discharge had been passed for the first time, on allowing vapour under saturation pressure (12 mm.) to stand in the apparatus (initially evacuated to 0.000 mm.), it was found that after 18 hours, the pressure of gas formed had attained to the order of 1 cm.

The seat of the effect was found to be in the X-ray tube; for, on removing the latter, the effect was greatly reduced. An attempt was then

made to remove the cause of the effect. The apparatus was steamed for two hours between T_1 and T_4 , and fresh mercury put in the manometers and traps. On now allowing vapour under saturation pressure to stand in the apparatus, the effect was found to be enormously reduced.

Initial pressure : 0·000 mm.

VAPOUR ADMITTED (UNDER SATURATION (12 MM.) PRESSURE).

Intervals of Time.	Pressures as per Gauge.
1 min.	0·001 min.
7	0·004
14	0·005
31	0·0045
51	0·0045

The seat of this minute remaining effect was found to be in the bulb of the McLeod gauge itself. This result is natural enough; for, during the process of steaming the apparatus, the gauge bulb, which afforded no exit for the steam, could not have been subjected to so thorough a cleansing as the other parts of the apparatus. In the course of the next few days, this residual effect disappeared.

The X-ray tube, after having been thoroughly steamed, was then refitted, the previous effect tested for, and found unrenewed.

Preparatory to repeating experiments on the passage of the discharge through water vapour, the discharge was passed for some time through two or three thousandths of a millimetre of air, pumping being at the same time kept up; the object being the driving out and removal of as much as possible of the gas which might be occluded in the walls of the tube and in the electrodes.

After this had been satisfactorily done, it was found that on allowing water vapour under its saturation pressure to stand in the apparatus, the pressure as indicated by the gauge began to increase steadily. The discharge, at the time, was not being passed. The previous effect, then, was once more present, and must have been brought about solely by the last passage of the discharge. On repeating the experiment, the effect increased in magnitude; and very shortly afterwards, on allowing vapour under its saturation pressure to stand in the apparatus, the pressure of gas formed after 15 hours, reached a value of the order of $1\frac{1}{2}$ cm. At the same time, the cathode had become incrustated with a greyish growth. Enough gas had been formed to allow of its being pumped out and

collected. About 3 cc. were collected over mercury and found to be inflammable.

These results seem to point to a reduction of the water vapour, probably by aluminium-mercury-couple, formed from the aluminium in the presence of mercury, or perhaps even of mercury vapour, hydrogen being liberated and the aluminium being converted into the hydrate AlO_3H_3 . This reduction, however, apparently cannot take place unless the discharge has passed at least once through the tube; but once it has been brought about, it increases rapidly in magnitude.

Experiments were made which showed that the presence of aluminium in contact with mercury vapour was solely responsible for the supposed reduction effect on the water vapour, but that the passage of a discharge at least once was always necessary before the effect occurred. Water vapour suffered no reduction if admitted into a new tube. A point of some interest noted in the course of these experiments was that the aluminium in the tube need not necessarily form one of the electrodes; indeed it might even be quite removed from the direct path of the discharge.

Elimination of the Reduction Effect.—With a view to eliminating the reduction effect, a discharge tube containing no aluminium, about 13 cm. long, with two platinum wire electrodes, was fitted.

Vapour under its saturation pressure was allowed to stand in the apparatus on three successive occasions, and any reduction effect found to be totally absent.

On passing the discharge through vapour under 0.9 mm. pressure, the tube being free of any platinum-black, the McLeod gauge indicated a small increase in pressure from 0.015 mm. to 0.017 mm. (Curve 1.)

On repeating the experiment the results were as follows:—

Initial pressure: 0.000 mm.

11.27 A.M. SAME QUANTITY H_2O ADMITTED, AND DISCHARGE PASSED CONTINUOUSLY.

Time.	Pressure as per Gauge.
11.32 a.m.	0.047 mm.
11.39	0.030
11.46	0.020
11.54	0.021

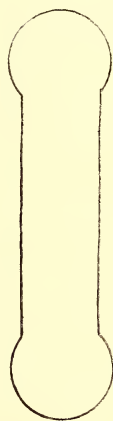
(Curve 2.)

During the latter part of the experiment the cathode was at a red heat, and intense disintegration was taking place. The tube, in the neighbourhood of the electrodes, more especially the cathode, was now very black.

The above experiments were repeated, with the tube in the same condition, on three occasions when the temperature conditions were much the same. Curve 3 shows how the pressure as indicated by the McLeod gauge varied with time on each occasion. The pressure increased rapidly during the first few minutes to a maximum value, after which it fell at a diminishing rate. Curve 4 shows a case where the P_2O_5 bulb was put into connection with the remainder of the apparatus immediately after this maximum value of the pressure had been attained. It serves to compare the action of the P_2O_5 with that of the agency responsible in these last experiments for the falling off of the pressure with time.

This agency must be the platinum-black on the walls of the tube; for the falling off of pressure with time was absent when the tube was clean, and increased simultaneously with the formation of the deposit. That the seat of the effect was actually in the discharge tube was verified experimentally.

Experiments with the Electrodeless Discharge.—In order to remove the effect apparently due to the platinum-black, a tube with no electrodes was substituted for the last discharge tube. The tube, 15 cm. in length, was made of 1.5 cm.-bore soda-glass tubing. The ends were knob-shaped and covered with tinfoil caps to which were connected the wires from the induction coil.



The gases from the walls of the tube were driven out and removed by pumping at intervals while the discharge was passed through air under a pressure of a few thousandths of a mm. Hg. During this process a belt of brownish-black coloration appeared near the cathode extremity of the tube. The discharge was passed through vapour under 0.9 mm. pressure on three successive occasions, the temperature conditions being very similar (about 14° C.). Curve 5 shows how the pressure as registered by the McLeod gauge varied with the time on each occasion. During the first few minutes there was a rapid increase to 0.08 mm., after which there was a falling off at a diminishing rate. The results are very similar to those obtained when corresponding experiments were conducted with the previous tube. The coloration on the walls of the tube remained throughout the experiments.

The discharge was passed through vapour under 1.7 mm. pressure, the temperature being 14.5° C. As before, the pressure increased to a maximum, and then decreased at a diminishing rate; but the

maximum in this case was greater while the decrease in the pressure was less. (Curve 6.)

As the pressure of gas produced approached its maximum value the coloration on the tube began to disappear; at the end of the experiment, however, the greater portion was still present.

The discharge was passed through vapour under 2.6 mm pressure, the temperature being 14.5° C. The pressure again immediately began to increase, while the coloration, from the instant of starting the discharge, disappeared rapidly. When the pressure as indicated by the gauge had reached the value 0.308 mm., the last traces of colour had vanished. After this point the pressure did not vary much. (Curve 7.) Three and a half hours afterwards (the discharge having passed continuously) the pressure as indicated by the gauge was 0.307 mm., while the tube had remained perfectly free of coloration. In this case, then, we have again a rise in pressure to a maximum value; but the maximum is permanent; there is no subsequent falling off of the pressure.

The tube being now free of coloration, the above experiments were repeated:

The discharge was passed through vapour under 0.9 mm. pressure, (temperature = 14° C.). The pressure increased to a maximum value of 0.07 mm., after which it did not appreciably diminish. Until the maximum had been reached, the tube remained perfectly free of coloration. After this faint traces of returning coloration began to appear. (Curve 8.)

The discharge was passed through the same quantity of vapour. The coloration became more apparent, and the pressure increased to a higher maximum than before, after which it diminished for a short time. (Curve 9.)

The discharge was passed through vapour under a pressure of 2.7 mm. As in the previous parallel case, the coloration immediately began to vanish, while the pressure as indicated by the gauge rose to a maximum and permanent value of 0.34 mm., when the last traces of coloration disappeared.

The coloration, then, occurred if the pressure under which vapour was admitted was less than about 2.5 mm. If the coloration was present and the discharge was passed through vapour under a pressure just greater than 2.5 mm., the coloration disappeared, while the pressure of gas in the apparatus increased to a permanent maximum value. Further, as the following results show, if the discharge is passed through the same quantity of vapour, while the tube was free of colour, the pressure, as before, increased to a permanent maximum value, while there was at no time any coloration.

Tube free of colour.

Temperature $14\cdot3^{\circ}\text{C}$.

DISCHARGE PASSED THROUGH VAPOUR UNDER PRESSURE OF $2\cdot6\text{ mm}$.

Intervals of Time.	Pressure as per Gauge.
1 min.	0·037 mm.
3	0·175
6	0·234
9	0·289
13	0·325
18	0·339
21	0·338
40	0·339

Discharge stopped.

Tube free of colour.

It appears reasonable to suppose that this coloration was the result of chemical action of cathode rays on the glass. According to J. J. Thomson ("Conduction of Electricity through Gases," 2nd edition, p. 623) such coloration rapidly disappears on mere exposure to water vapour. In the present instance, however, the passage of a discharge through the water vapour was found to be essential for the vanishing of the coloration; *e.g.*, the pressure of gas in the apparatus being initially $0\cdot000\text{ mm}$., vapour under its saturation pressure (12 mm .) was admitted and allowed to stand for twenty hours. At the end of this time there was no apparent diminution in the coloration, while the McLeod gauge indicated a pressure of gas of $0\cdot001\text{ mm}$., showing that no appreciable dissociation or reduction of the vapour had taken place. On passing the discharge, however, a considerable amount of the coloration had already disappeared at the end of two minutes and was fast continuing to do so.

On passing the discharge through vapour under pressures greater than about $2\cdot5\text{ mm}$., the pressure corresponding to unstability of the coloration, the gauge readings indicated increases in pressure to permanent maximum values. (Curves 10, 11, 12, 13, 14.) These maximum values did not become continually greater as the pressure of vapour admitted became greater. They differed little from one another except when the pressure of vapour admitted approached saturation pressure ($11\text{ to }12\text{ mm}$.).

Thus :—

Pressure under which Vapour was admitted.	Maximum Pressure of Gas produced.
2.6 mm.	0.340 mm.
4.0	0.306
7.1	0.354
8.0	0.41
8.8	0.44
10.0	1.08
12.0 (Sat. press.)	2.85

The time taken for the pressures to attain to their maximum values increased as the pressure under which the vapour was admitted became greater—a result to be expected, for the more water vapour is initially introduced the greater will be the hindrance to diffusion of the gas produced through the apparatus, and, consequently, the longer will be the time for a state of equilibrium to be set up. The temperature during these observations was in the neighbourhood of 14° C., but not particularly constant.

A series of experiments was made to determine how these maximum pressures, in addition to depending on the pressure under which the vapour stood initially in the apparatus, depended on the temperature. These experiments were conducted with a new tube, similar in construction to the last, although differing slightly in its dimensions. The renewal of the tube was necessary owing to the breaking down of the previous one, due, presumably, to its perforation by the discharge. The gases from the walls of the tube were driven out as before; and, as before, a belt of colour again formed near the centre of the tube during the process. Experiments identical with those conducted with the previous tube were made, and served to confirm the previous results. The maximum pressure of gas formed increased with the pressure under which vapour was introduced, up to the point of disappearance of the coloration. In this case, however, it was necessary to pass the discharge through vapour under 4 mm. pressure before the last traces of colour completely vanished. Also, as before, when the pressure under which the vapour was admitted was less than 4 mm., the pressure of gas formed, after reaching its maximum value, diminished at a decreasing rate; *i.e.*, provided some coloration was present, the maximum pressures of gas formed was followed by a diminution at a decreasing rate. Curves 15, 16, 17, 18, 19, 20 show how the pressure of gas formed by the passage of the discharge varied with the time, when the discharge was passed through vapour under various pressures up to 4 mm.

The discharge was passed through vapour under various pressures, ranging to saturation pressure, for certain temperatures, the method of procedure being as follows: After exhausting the apparatus included between the traps T_1 and J to 0.000 mm., the requisite amount of vapour was introduced, and trap T_4 closed to separate the discharge tube, McLeod gauge, &c., from any moisture that might rise to the surface of the mercury at b during the course of the experiment. At the end of each experiment, immediately after the discharge had been stopped, the water vapour was absorbed, and the apparatus again exhausted to prevent any appreciable occlusion of gas in the walls of the tube, which would be driven out by the discharge in the next experiment, and so cause error. In order to maintain the temperature constant the days were chosen cooler by two or three degrees than the required temperature, and the temperature kept up by regulating a number of glow-lamps. In this way it was found possible to prevent the temperature from varying by more than 0.1°C .

Following is a series of experiments conducted at the temperature 19.8°C . The series is typical of others:—

(1) AT 1.0 P.M. DISCHARGE PASSED THROUGH H_2O UNDER 0.6 MM. PRESSURE.

Times.	Pressures.	Temperature.	Remarks.
1.1 p.m.	0.050 mm.	19.80°C .	Faint green fluorescence.
1.3	0.060	19.80	—
1.5	0.055	19.80	Appearance of coloration.
1.10	0.047	19.80	—
1.14	0.041	19.80	—
1.36	0.036	19.80	Signs of more pronounced fluorescence.

(2) AT 3.19 P.M. DISCHARGE PASSED THROUGH H_2O UNDER 2.1 MM. PRESSURE.

Times.	Pressures.	Temperature.	Remarks.
3.21 p.m.	0.095 mm.	19.80°C .	Very narrow striations with faint fluorescence.
3.26	0.196	19.85	—
3.29	0.217	19.85	—
3.32	0.220	19.85	Striations less distinct.
3.40	0.219	19.85	—
3.52	0.217	19.80	—
4.2	0.213	19.80	—
4.11	0.208	19.80	Coloration still present.

(3) AT 4.20 P.M. DISCHARGE PASSED THROUGH H_2O UNDER 3.5 MM. PRESSURE.

Times.	Pressures.	Temperature.	Remarks.
4.30 p.m.	0.243 mm.	19.85° C.	No distinct striations.
4.40	0.290	19.85	Coloration began to disappear immediately. At
4.50	0.301	19.85	4.40 only a faint trace
4.59	0.310	19.80	remained.
5.14	0.306	19.80	Last trace of coloration disappeared.

(4) AT 2.3. P.M. DISCHARGE PASSED THROUGH H_2O UNDER 3.7 MM. PRESSURE.

Times.	Pressures.	Temperature.	Remarks.
2.6 p.m.	0.091 mm.	19.85° C.	—
2.12	0.221	19.80	—
2.22	0.282	19.75	—
2.34	0.302	19.80	—
2.42	0.301	19.85	No return of coloration at any time.

(5) AT 2.55 A.M. DISCHARGE PASSED THROUGH H_2O UNDER 4.9 PRESSURE.

Times.	Pressures.	Temperature.
3.6 p.m.	0.215 mm.	19.80° C.
3.11	0.256	19.80
3.17	0.274	19.80
3.27	0.283	19.80
3.34	0.282	19.80

(6) AT 11.30 A.M. DISCHARGE PASSED THROUGH H_2O UNDER 5 MM. PRESSURE.

Times.	Pressures.	Temperature.
11.42 a.m.	0.188 mm.	19.70° C.
11.49	0.228	19.80
11.58	0.243	19.85
12.8 noon	0.253	19.85
12.23	0.256	19.75
12.32	0.263	19.70
12.56	0.279	19.75
1.0 p.m.	0.279	19.80

(7) AT 3.46 P.M. DISCHARGE PASSED THROUGH H_2O UNDER 6.2 MM. PRESSURE.

Times.	Pressures.	Temperature.
3.59 p.m.	0.184 mm.	19.70° C.
4.11	0.227	19.85
4.22	0.228	19.80
4.28	0.227	19.80

(8) AT 2.6 P.M. DISCHARGE PASSED THROUGH H_2O UNDER 8.3 MM. PRESSURE.

Times.	Pressures.	Temperature.
2.13 p.m.	0.079 mm.	19.80° C.
2.17	0.112	19.80
2.31	0.168	19.80
2.47	0.182	19.85
3.4	0.188	19.85
3.10	0.188	19.85

